13.E: Variational Methods (Exercises)

1. Consider a hydrogen-like atom consisting of a single electron of charge \((-e)\) orbiting about a massive nucleus of charge \((Z, e)\) (where \(|Z| > 0\)). The eigenstates of the Hamiltonian can be labelled by the conventional quantum numbers \((n), (l), \) and \((m)\).

   a. Show that the energy levels are \(E_n = \frac{Z^2 E_0}{n^2}\), where \(E_0\) is the ground-state energy of a conventional hydrogen atom.

   b. Demonstrate that the first few properly normalized radial wavefunctions, \(R_{n,l}(r)\), take the form:

   \[
   \begin{aligned}
   R_{1,0}(r) &= \frac{2 Z^{3/2}}{a_0^{3/2}} \exp\left(-\frac{Z r}{a_0}\right), \\
   R_{2,0}(r) &= \frac{2 Z^{3/2}}{(2 a_0)^{3/2}} \left(1 - \frac{Z r}{2 a_0}\right) \exp\left(-\frac{Z r}{2 a_0}\right), \\
   R_{2,1}(r) &= \frac{Z^{3/2}}{\sqrt{3} (2 a_0)^{3/2}} \frac{Z r}{a_0} \exp\left(-\frac{Z r}{2 a_0}\right).
   \end{aligned}
   \]

   where \(a_0\) is the Bohr radius.

2. Given that the ground-state energy of a helium atom is \(-78.98\, \text{eV}\), deduce that the ground-state ionization energy (i.e., the minimum energy that must be supplied to remove a single electron from the atom in the ground-state) is \(-24.56\, \text{eV}\).

3. Consider a helium atom in which both electrons are in the \(n=2, l=1, m=0\) state (i.e., the \(2p\) state). Use the techniques of Section 1.3 to obtain the following estimate for the energy of this state: \(E(2p, 2p) = -2 + \frac{3 \cdot 31}{2^7} E_0 = -17.33\, \text{eV}\). Note that this energy lies well above the energy of the ground-state of singly-ionized helium, which is \(E_{\text{He}^+} = 4 E_0 = -54.42\, \text{eV}\). This means that a helium atom excited to the \(2p, 2p\) state has the option of decaying into a free electron and a singly-ionized helium ion, with the energy of the ejected electron determined by energy conservation. This process is known as autoionization.

4. Consider the general energy eigenvalue problem \(H \psi = E \psi\). Suppose that \(\psi = E \psi\) is a trial solution to the previous equation that is not properly normalized. Prove that \(E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}\), where \(E_0\) is the lowest energy eigenvalue.

5. Consider a particle of mass \(m\) moving in the one-dimensional potential \(V(x) = \lambda x^4\) where \(\lambda > 0\). Let \(|\psi_0(x)\rangle = \frac{\alpha^{1/2}}{\pi^{1/4}} \exp\left(-\alpha x^2/2\right)\) and \(|\psi_1(x)\rangle = \frac{\sqrt{2} \beta^{3/2}}{\pi^{1/4}} x \exp\left(-\beta x^2/2\right)\). Verify that these wavefunctions are properly normalized. Use the variational
principle, combined with the plausible trial wavefunctions $\langle \psi_0(x) \rangle$ and $\langle \psi_1(x) \rangle$ (these wavefunctions are, in fact, the exact ground-state and first-excited-state wavefunctions for a particle moving in the potential $\langle \lambda x^2 \rangle$) to obtain the following estimates for the energies of the ground state, and the first excited state, of the system: $E_0 = \frac{3^{4/3}}{4} \left( \frac{\hbar^2}{2m} \right)^{2/3} \lambda^{1/3} = 1.082 \left( \frac{\hbar^2}{2m} \right)^{2/3} \lambda^{1/3}$, $E_1 = 3.847 \left( \frac{\hbar^2}{2m} \right)^{2/3} \lambda^{1/3}$. The exact numerical factors that should appear in the previous two equations are $(1.060)$ and $(3.800)$, respectively. Hence, it is clear that our approximation to $E_0$ and $E_1$ are fairly accurate.

6. Use the variational technique outlined in Section 1.3 to derive the following estimate the ground-state energy of a two-electron atom with nuclear charge $Z_0 e$ in the spin-singlet state: $E = \frac{(16Z_0 - 5)^2}{2^7} E_0$, where $E_0$ is the hydrogen ground-state energy. For the case of a negative hydrogen ion (i.e., $Z_0 = 1$), this formula gives $E = -12.86 \langle \text{eV} \rangle$. The experimental value of this energy is $E = -14.36 \langle \text{eV} \rangle$. For the case of a singly-ionized lithium ion (i.e., $Z_0 = 2$), the previous formula gives $E = -196.54 \langle \text{eV} \rangle$. The experimental value of this energy is $E = -198.09 \langle \text{eV} \rangle$.

7. It can be seen from Section 1.3, as well as the previous exercise, that the variational technique described in Section 1.3 yields approximations to the ground-state energies of two-electron atoms in the spin-singlet state that are approximately $1.5 \langle \text{eV} \rangle$ too high. This is not a particular problem for the helium atom, or the singly-ionized lithium ion. However, for the negative hydrogen ion, our estimate for the ground-state energy, $E = -12.86 \langle \text{eV} \rangle$, is slightly higher than the ground-state energy of a neutral hydrogen atom, $E = -13.61 \langle \text{eV} \rangle$, giving the erroneous impression that it is not energetically favorable for a neutral hydrogen atom to absorb an additional electron to form a negative hydrogen ion (i.e., that the negative hydrogen ion has a negative binding energy).

Table associated with Exercise [ex13.7].

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$\epsilon$</th>
<th>$Z_1$</th>
<th>$Z_2$</th>
<th>$E \langle \text{eV} \rangle$</th>
<th>$E_{\text{expt}} \langle \text{eV} \rangle$</th>
</tr>
</thead>
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<tr>
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<td>(1.04)</td>
<td>(0.28)</td>
<td>-13.97</td>
<td>-14.35</td>
</tr>
<tr>
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<td>+1</td>
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<td>(1.19)</td>
<td>-78.25</td>
<td>-78.98</td>
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<td>-1</td>
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<td>(0.32)</td>
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<td>(2.08)</td>
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<tr>
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<td>-1</td>
<td>(2.93)</td>
<td>(0.60)</td>
<td>-138.01</td>
<td>-139.06</td>
</tr>
</tbody>
</table>

Obviously, we need to perform a more accurate calculation for the case of a negative hydrogen ion. Following Chandrasekhar, let us adopt the following trial wavefunction: $\phi({\bf r}_1, {\bf r}_2) = \frac{1}{\sqrt{2}} \left[ \psi_1({\bf r}_1) \psi_2({\bf r}_2) + \epsilon \psi_2({\bf r}_1) \psi_1({\bf r}_2) \right]$, where $\psi_1({\bf r}) = \frac{1}{\sqrt{\pi}} \left( \frac{Z_1}{a_0} \right)^{3/2} \exp \left( -\frac{Z_1 r}{a_0} \right)$ and $\psi_2({\bf r}) = \frac{1}{\sqrt{\pi}} \left( \frac{Z_2}{a_0} \right)^{3/2} \exp \left( -\frac{Z_2 r}{a_0} \right)$. Here, $r = |{\bf r}|$, $a_0$ is the Bohr radius, and $Z_1$, $Z_2$ are adjustable parameters. Moreover, $\epsilon$ takes the values $+1$ and $-1$ for the spin-singlet and spin-triplet states, respectively. Given that the Hamiltonian of a two-electron atom of nuclear charge $Z e$ is $H = \frac{1}{2} \left[ \frac{\hbar^2}{2m} \left( \frac{\hbar^2}{2m} \right)^{2/3} \lambda^{1/3} \right]$, we have $E = \frac{(16Z - 5)^2}{2^7} E_0$. The experimental value is $E = -14.36 \langle \text{eV} \rangle$. For the case of a singly-ionized lithium ion (i.e., $Z = 3$), the previous formula gives $E = -198.09 \langle \text{eV} \rangle$. The experimental value is $E = -198.09 \langle \text{eV} \rangle$. It can be seen from Section 1.3, as well as the previous exercise, that the variational technique described in Section 1.3 yields approximations to the ground-state energies of two-electron atoms in the spin-singlet state that are approximately $1.5 \langle \text{eV} \rangle$ too high. This is not a particular problem for the helium atom, or the singly-ionized lithium ion. However, for the negative hydrogen ion, our estimate for the ground-state energy, $E = -12.86 \langle \text{eV} \rangle$, is slightly higher than the ground-state energy of a neutral hydrogen atom, $E = -13.61 \langle \text{eV} \rangle$, giving the erroneous impression that it is not energetically favorable for a neutral hydrogen atom to absorb an additional electron to form a negative hydrogen ion (i.e., that the negative hydrogen ion has a negative binding energy).
\[2\,m_e + \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{Z\,e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}},\] show that the expectation value of \(H\) (i.e., \(\langle H \rangle = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}\)) is
\[
\frac{\langle H \rangle}{|E_0|} = \left[ x^8 - 2Zx^7 - \frac{1}{2}x^6y^2 + \frac{1}{2}x^5y^2 + \frac{1}{8}x^3y^4 - \epsilon(2Z - \frac{5}{8})x^2y^6 + \frac{1}{2}\epsilon y^8 \right] / \left( x^6 + \epsilon y^6 \right),
\]
where \(E_0\) is the hydrogen ground-state energy, \(x = Z_1 + Z_2\), and \(y = 2\sqrt{Z_1Z_2}\). We now need to minimize \(\langle \phi | H | \phi \rangle\) with respect to variations in \(Z_1\) and \(Z_2\) to obtain an estimate for the ground-state energy. Unfortunately, this can only be achieved numerically.

Table [table1] shows the numerically determined values of \(\langle Z_1 \rangle\) and \(\langle Z_2 \rangle\) that minimize \(\langle \phi | H | \phi \rangle\) for various choices of \(Z\) and \(\epsilon\). The table also shows the estimate for the ground-state energy of the negative hydrogen ion, which demonstrates that the negative hydrogen ion has a positive (albeit, small) binding energy. Incidentally, the case \(Z = 2\), \(\epsilon = -1\) yields a good estimate for the energy of the lowest-energy spin-triplet state of a helium atom (i.e., the \((1s,2s)\) spin-triplet state).

8. It can be shown, numerically, that the previous function attains its minimum value, \(F_+ = -1.173\), when \((Z = 1.238)\) and \((y = 2.480)\). This leads to predictions for the equilibrium separation between the two protons, and the binding energy of the molecule, of \(R_0 = (2.480/1.238)a_0\), \(a_0 = 2.003\), \(1.06\times 10^{-10}m\) and \(E_{\text{bind}} = 0.173|E_0| = 2.35\text{ eV}\), respectively. (See Figure [fh2pa].) These values are far closer to the experimentally determined values, \(R_0 = 1.06\times 10^{-10}m\) and \(E_{\text{bind}} = 2.8\text{ eV}\), than those derived in Section 1.4. [ex9.23]

Contributors and Attributions

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